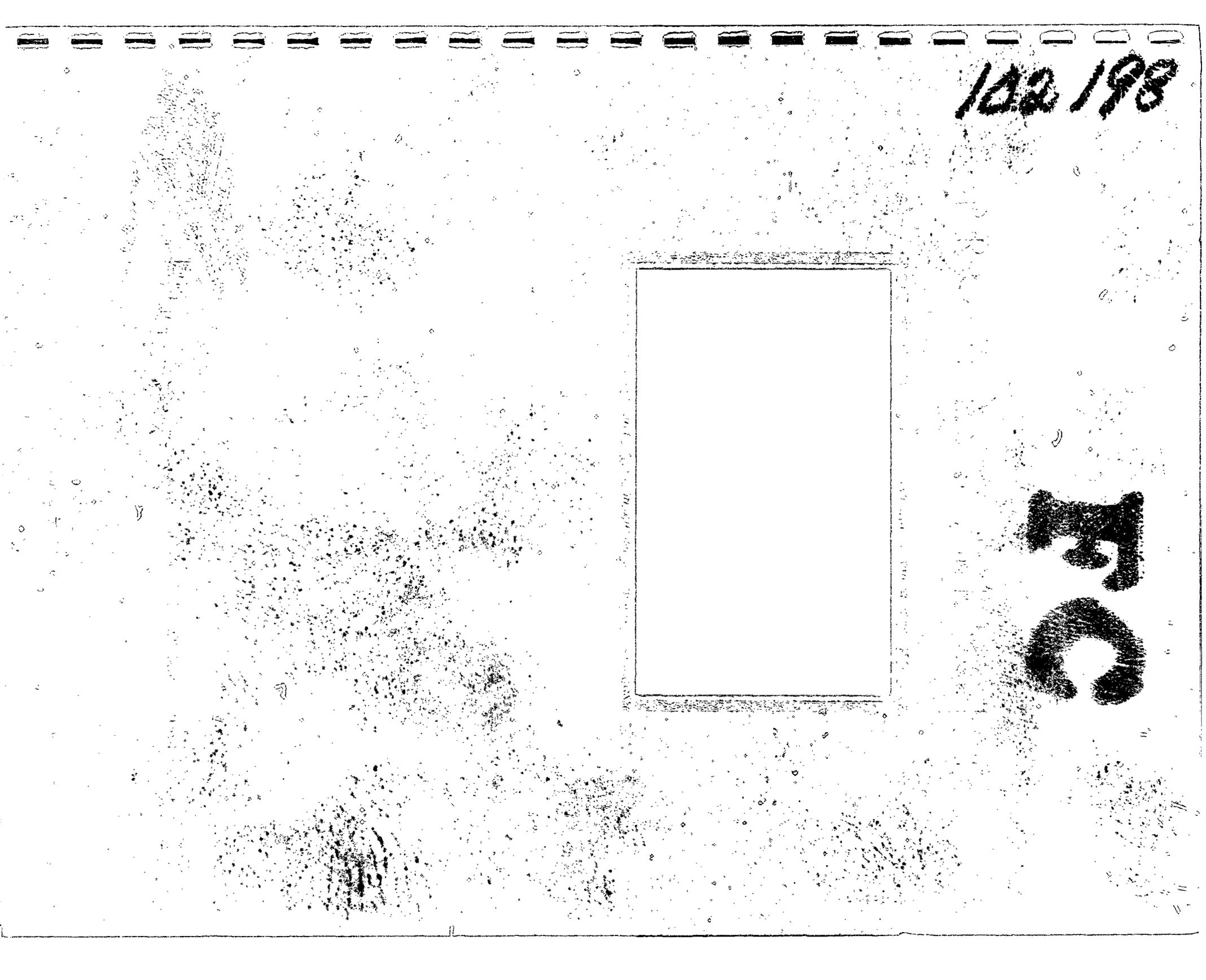

STATUS REPORT NO. 6

on

THE PHYSICAL AND CHEMICAL PROPERTIES OF TITANIUM BROMIDES AND TITANIUM IODIDES

Contract No. Nonr-1120(00)

to

HEAD, METALLURGY BRANCH
OFFICE OF NAVAL RESEARCH

July 1, 1955

by

J. M. Blocher, Jr., N. D. Veigel,
E. H. Hall, and I. E. Campbell

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July 29, 1955

Mr. W. C. Arsem
Metallurgy Branch
Office of Naval Research
Department of the Navy
Washington 25, D. C.

Dear Mr. Arsem:

Contract No. Nonr-1120(00)

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Sincerely yours,

I. E. Campbell

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THE PHYSICAL AND CHEMICAL PROPERTIES OF TITANIUM BROMIDES AND TITANIUM IODIDES

by

J. M. Blocher, Jr., N. D. Veigel,
E. H. Hall, and I. E. Campbell

SUMMARY

Data obtained in a study of the mercury reduction of titanium tetrabromide were used to calculate the difference in the heats of formation of $TiBr_4(s)$ and $TiBr_3(s)$. After confirmation, these results will be combined with the heat of formation of $TiBr_4(s)$ now being determined at the National Bureau of Standards to obtain the value for the heat of formation of $TiBr_3(s)$. Tentative values are included in this report.

Tests are being made of modifications of the apparatus for the determination of the disproportionation pressure of $TiBr_3$ in order that reliable pressure-temperature-composition data can be obtained which will be combined with the above to give the heat of formation of $TiBr_2(s)$.

INTRODUCTION

As initially planned, the thermodynamic properties of the titanium bromides were to have been determined by studying the equilibria:

$$TiBr_3(s) + 1/2\ Hg_2Br_2(s) = Hg(\ell) + TiBr_4(g) \qquad (1)$$

$$2TiBr_3(s) = TiBr_4(g) + TiBr_2(s) \qquad (2)$$

$$3TiBr_2(s) = 2TiBr_3(g) + Ti(s)\ . \qquad (3)$$

Acceptable values of the heat of formation of Hg_2Br_2 were available*, and exploratory work with the mercury-reduction reaction (Equation 1) indicated that reliable experimental results could be obtained.

The disproportionation of $TiBr_3$ (Equation 2) had also been studied. However, this system is not "well behaved" and further work will be necessary to establish a reliable value of the heat of disproportionation.

*Circular 500, National Bureau of Standards.

The disproportionation of $TiBr_2$ (Equation 3) was to have been studied to complete the determination of the relative thermodynamic properties of the titanium bromides. However, this system would undoubtedly be still more difficult to work with than the tribromide disproportionation. Therefore, it was desirable that another reaction be chosen to complete the picture.

Fortunately, reliable values for the heat of formation of $TiBr_4$ should result from the work in progress at the National Bureau of Standards by E. J. Prosen and his associates*. With this information available, only the heats of reaction of Equations (1) and (2) will be necessary to determine the heats of formation of the three titanium bromides.

Details of recent work on the tribromide disproportionation were given in Status Report No. 5. During the present report period, tests were made of several techniques for obtaining reliable pressure-temperature-composition data. However, no experimental measurements were made. The major effort during the report period was concentrated on the determination of the equilibrium $TiBr_4$ pressure in the mercury reduction reaction (Equation 1).

MERCURY REDUCTION OF TITANIUM TETRABROMIDE

Experimental

To identify the solid phases in equilibrium with liquid mercury and $TiBr_4$ vapor, samples of the reaction product were subjected to X-ray-diffraction analysis at temperatures from 150° to 250°C. at which the equilibrium pressure of $TiBr_4$ is easily measured. $TiBr_3$ and Hg_2Br_2 were identified as solid phases and no unidentified lines remained which might indicate complicating factors.

Measurements of the equilibrium pressure were made in the apparatus shown in Figure 1. The cell was carefully cleaned and outgassed and then charged with mercury by distillation from a reservoir attached at Point A. A small amount of pure $TiBr_4$ was also distilled into the cell and allowed to react with the mercury to form a surface coating of Hg_2Br_2 and $TiBr_3$, after which the cell was sealed off at A and separated from the filling apparatus. The purpose of the flexible rubber tubing connecting the cell to the vacuum and controlled-pressure system was to permit outgassing by inverting the cell and evacuating the system.

The cell was used as a null indicator, the pressure above the bromides being balanced by a measured pressure of inert gas which was varied until

*Private communication, March 7, 1955.

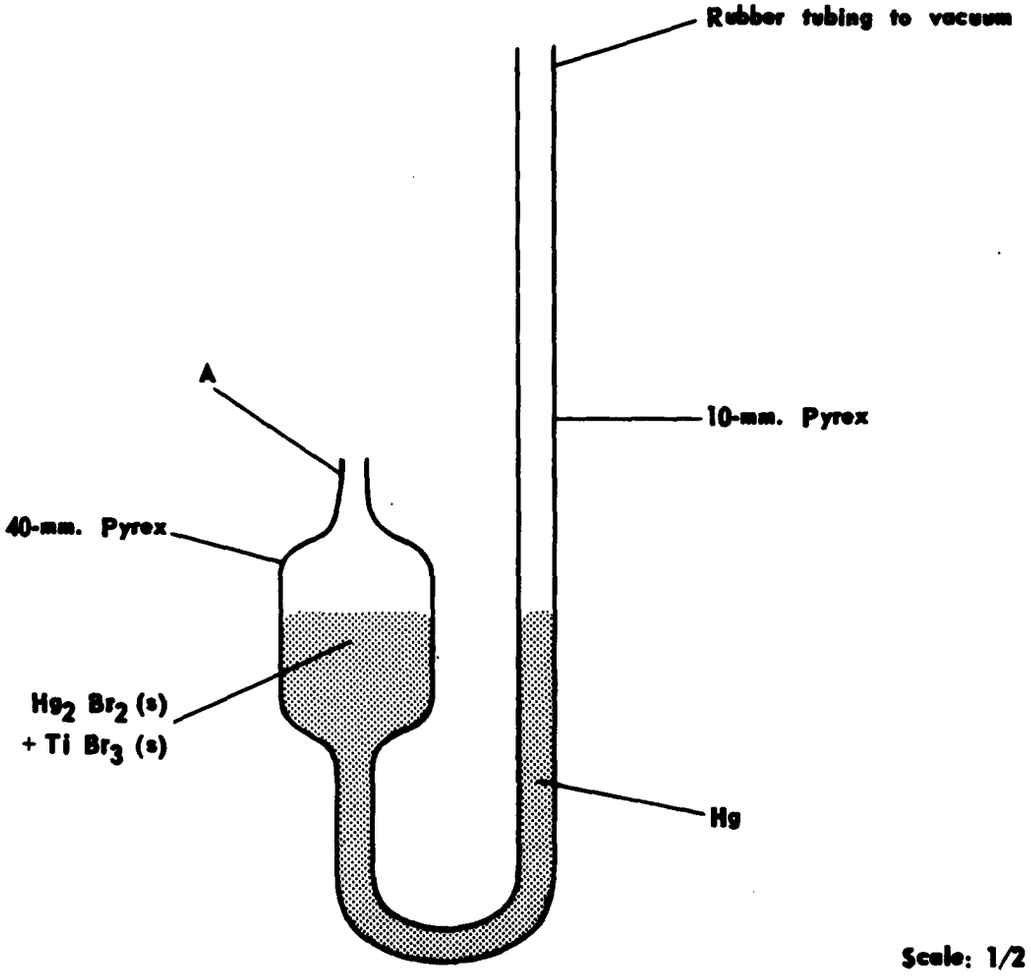

FIGURE 1. MERCURY REDUCTION CELL

the mercury level in the 10-mm tube was returned to the position occupied at zero pressure differential. Data for the correction for the thermal expansion of mercury were obtained with mercury alone in the cell by determining the mercury level in the 10-mm tubing as a function of temperature under zero pressure differential. As a check on the reliability of the technique, and of the prediction that the partial pressure of $HgBr_2(g)$ is negligible*, the cell was charged with mercury and bromine to form a scum of Hg_2Br_2 over the mercury surface. The pressure-temperature data given in Table 1 indicate that only the partial pressure of mercury is significant although there appears to be a small systematic error in the experimental values. This saturated mercury vapor pressure is exerted, along with the equilibrium $TiBr_4$ pressure, in the mercury-reduction reaction, and must be subtracted from the total pressure to obtain the partial pressure of $TiBr_4$.

The cell was thermostatted to ±0.2°C. in a salt bath whose temperature was measured by a calibrated Chromel-Alumel thermocouple. The data obtained with two separate preparations (Runs A and B) are given in Table 2 and Figure 2.

Discussion

In order to extrapolate the experimental data to 298.2°K., it is necessary to obtain a value for the ΔC_p of reaction. Unfortunately, reliable values for the heat capacities of $TiBr_3$ and Hg_2Br_2 are not available. However, values obtained by estimation should be entirely satisfactory for this purpose. The heat capacity of Hg_2Br_2 was taken as the average (24.8 cal./mole/deg. at 298.2°K.) of those of Hg_2Cl_2 and Hg_2I_2 given in National Bureau of Standards Circular 500. The heat capacity of $TiBr_3$ (also 24.8 cal./mole/deg. at 298.2°K.) was estimated by adding 0.8 cal./deg./gram-atom to the heat capacity of $TiCl_3$ obtained by averaging the heat capacities given for VCl_3 and $AlCl_3$. The heat capacity of mercury is also given in Circular 500. That of $TiBr_4(g)$ was obtained by calculation from spectroscopic data as discussed previously**. The resulting value of $\Delta C_p = -6.5$ was taken to be constant over the temperature range of the measurements.

Owing to the uncertainty in the zero setting during Run A, together with the fact that the charge in the cell became depleted at higher temperatures, the values obtained in that run are shown only for purposes of indicating a rough check on the measurements of Run B. Treatment of the data from Run B gives, for Equation (1),

*Calculations based on the data given by Brewer (National Nuclear Energy Series, Vol. IV-19B, McGraw-Hill, 1950) indicate a $HgBr_2$ pressure, for example, of 0.13 mm. at 225°C.

**Status Report No. 3, October 1, 1954, p. 10.

TABLE 1. TOTAL PRESSURE OVER $Hg(\ell)$ AND $Hg_2Br_2(s)$

Temperature, °C.	P_{total},[a] mm. of Hg	$P_{Hg(g)}$,[b] mm. of Hg	$P_{total}-P_{Hg}$, mm. of Hg	$\frac{\Delta p}{p}$, %
236.5	52.3	51.6	0.7	1.35
238.1	54.4	54.0	0.5	0.93
246.2	67.3	67.3	0.0	0.0
254.5	83.9	83.7	0.2	0.24
257.9	91.7	91.2	0.5	0.55
274.1	137.1	136.4	0.7	0.52

(a) Observed pressure corrected for latitude, and for thermal expansion of mercury in the cell and in the manometer.

(b) Handbook of Chemistry and Physics, 35th Edition, Chemical Rubber Publishing Company (1953-54), page 2147.

TABLE 2. EQUILIBRIUM $TiBr_4$ PRESSURE IN MERCURY REDUCTION REACTION

Run[a]	Temperature, °K.	P_{TiBr_4}, mm. of Hg	Σ	-I
A	449.3	6.4	-	-
A	443.4	4.3	-	-
A	430.5	1.7	-	-
A	472.3	21.7	-	-
A	466.0	16.9	-	-
A	463.3	14.0	-	-
A	446.8	5.6	-	-
B	462.7	12.0	6.9166	91.4126
B	475.7	25.0	7.2745	91.4170
B	492.2	60.8	7.7089	91.4552
B	459.4	10.0	6.8272	91.4332
B	449.7	5.6	6.5450	91.4408
B	491.0	56.5	7.6738	91.4318
B	510.7	139.8	8.1253	91.3170
B	444.1	3.7	6.3474	91.3120
			Avg. =	$\overline{91.4024}$ ± 0.052

(a) Data listed in order taken.

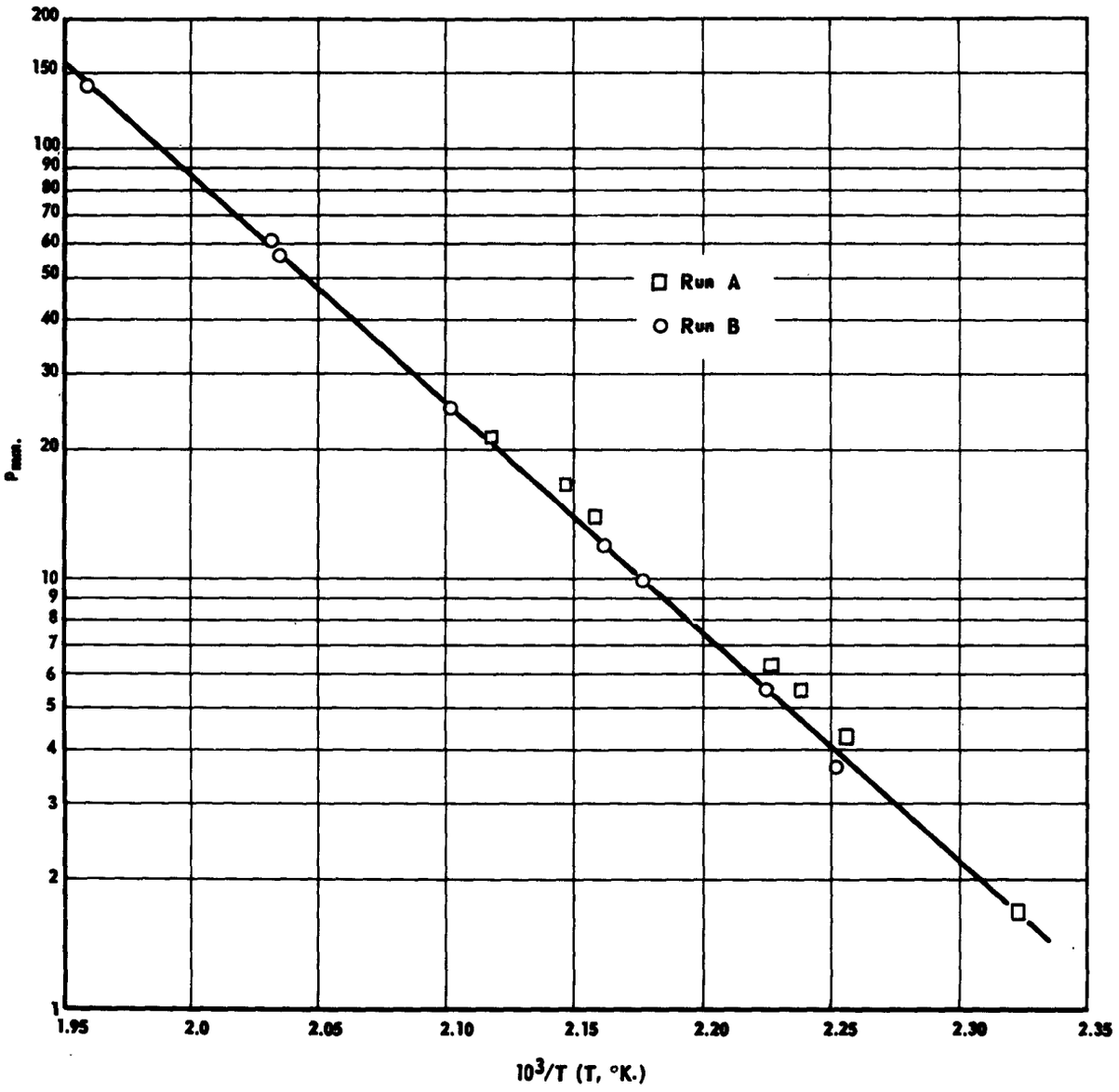

FIGURE 2. EQUILIBRIUM $TiBr_4$ PRESSURE IN MERCURY REDUCTION REACTION

$$\log p_{atm.} = -6044.9/T - 3.271 \log T + 19.979$$

$$\Delta H^{\circ}_{\bullet} = 27.66 \pm 0.21 \text{ kcal./mol}$$

$$\Delta H_{298.2} = 25.72 \pm 0.21 \text{ kcal./mol}$$

$$\Delta S_{298.2} = 47.86 \text{ e.u.}$$

Since entropy values can be estimated with much greater certainty than can heats of reaction, comparison of the entropy change obtained in the above work with that calculated from the best available information gives a good indication of the reliability of the experimental data. In calculating the entropy change for the reaction given by Equation (1), the values at 298.2°K. for Hg (ℓ) = 18.5 e.u. and 1/2 Hg_2Br_2(s) = 25.45 e.u. were taken from Circular 500. The value for $TiBr_4$(g) = 95.02 e.u. was calculated for spectroscopic data*, and that for $TiBr_3$(s) = 43 was taken from Brewer**. The difference between the experimental value, $\Delta S_{298.2} = 47.86$ e.u., and the calculated value, 45.07, is well within the ±7 e.u. uncertainty in the estimated entropy of $TiBr_3$.

The internal consistency of the data is indicated by the small deviation in the I values given in Table 2.

The above results may be combined with the heat of formation of Hg_2Br_2 (-49.42 kcal./mol.) and the heats of vaporization and fusion of $TiBr_4$ as determined at Battelle (13.02, and 3.06 kcal./mol., respectively, at 298.2***) to yield, for the reaction

$$1/2\ Br_2(\ell) + TiBr_3(s) = TiBr_4(s),\ \Delta H_{298.2} = -15.07 \text{ kcal./mol.}$$

E. J. Prosen and his associates at the National Bureau of Standards have recently obtained**** for

$$2Br_2(\ell) + Ti(\alpha) = TiBr_4(s),\ \Delta H_{298.2} = -147.8 \pm 1.3 \text{ kcal./mol.}$$

This may be combined with the above data to give the heat of formation of $TiBr_3$(s):

$$3/2\ Br_2(\ell) + Ti(\alpha) = TiBr_3(s),\ \Delta H_{298.2} = -132.7 \text{ kcal./mol.}$$

These results must be considered to be tentative, since additional measurements will be required to establish their precision. However, they are presented here with the thought that they may be useful to others.

*Status Report No. 3, October 1, 1954, p. 10.
**Brewer, loc. cit.
***Status Report No. 3, October 1, 1954, p. 10.
****Wagman, D. D., private communication, July 25, 1955.

FUTURE WORK

Additional data will be obtained for the equilibrium $TiBr_4$ pressure in the mercury reduction reaction.

The equipment used to determine the disproportionation pressure of TiBr3 will be modified to obtain more reliable pressure-temperature-composition data.

Original data are contained in Battelle Laboratory Record Book No. 10105, pp. 51-75.

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